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MINERAL REVIEW. II.

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MINERAL REVIEW. II.

By **RUTH WOODS**

The present issue will review the biological significance of sulfur; iodine, fluorine, and bromine; iron and copper; cobalt; and zinc.

Sulfur:

Sulfur is present in every cell of the body mainly as a constituent of the proteins. It is present also in certain of the carbohydrates and fats and in certain biologically important materials. About one-half of the body sulfur occurs in the muscles, about one-eighth each in the skeleton and skin; the remainder is distributed in varying amounts throughout the rest of the body. Most of the dietary sulfur is organic sulfur, occurring in the amino acids, methionine and cystine.

Sulfur Compounds in Body: The biological role of sulfur in the body has not been clearly defined. It is involved in numerous discrete physiological mechanisms, but not much is known concerning the behavior of sulfur in these mechanisms or the possible interrelations, if any, which these mechanisms may have with each other. The significance of sulfur in the body may be related to its occurrence in a number of biologically important materials.

The amino acids *methionine* and *cystine* are sulfur compounds which are important in both animal and human nutrition. Methionine has been shown to be nutritionally indispensable for man and animals. Cystine is an important constituent of the keratin proteins which occur in nails, wool, skin and hair. The methionine-cystine ratio of the diet has been shown to be an important factor in the growth of experimental animals. Investigation into the intermediate metabolism of methionine and cystine involving the newly recognized biological mechanism of transmethylation has contributed to the development of important new concepts in metabolism.*

The vitamin, *thiamine,* and the related enzyme, *cocarboxylase,* contain sulfur as a component of the thiazole ring.

Glutathione is a sulfur-containing compound which, because of its oxidation-reduction properties, is believed to play an important part in biological oxidations.

Other important sulfur-containing compounds are the hormone, *insulin; thioneine,* a constituent of blood; *taurine,* a protein derivative resulting from

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**cf. Borden's Review of Nutrition Research,* October, 1942—"Labile Methyl Groups," and September, 1946—"Labile Methyl Groups—New Findings."

the oxidation of bile acids; the *melanin pigments* of skin and hair; various *mercaptic acids,* important in detoxification mechanisms; and thiocyanates, compounds of sulfur and the cyanides, which occur in traces in blood, saliva (particularly in that of smokers), other secretions and urine. The *sulfhydryl radical* (SH) in many of these compounds is believed to be an important factor in influencing their behavior.

Requirements: Because it is a constituent of many important biological compounds and of the proteins which comprise the body tissues, sulfur is required by all living animals. The quantitative requirement is not a matter of nutritional concern, particularly if the protein intake of the diet is adequate. Proteins vary greatly in their sulfur content. The lactalbumin of milk contains 1.73 per cent of sulfur; wheat, 1.03 per cent; casein 0.80 percent; gelatin, 0.20 per cent. Wool and human hair are very rich in sulfur, the former containing about 3½ per cent sulfur and hair, particularly red hair, over 5 per cent.

Sources: Important food sources of sulfur are milk, whole wheat, oatmeal, eggs, lean beef, peas and beans.

Iodine:

Iodine occurs in small amounts in all of the earth's rocks, soils, dusts and waters. The iodine in sea water is absorbed and concentrated by seaweed; it is also found in sponges. Although these two materials were used empirically centuries ago for the treatment of simple goiter, the existence of the element iodine was not discovered until the 19th century. In the animal body iodine is concentrated almost entirely in the thyroid gland; small amounts occur in the blood and other tissues.

Function: The physiological importance of iodine is tied up with its occurrence as a major constituent (65 per cent) of thyroxin, the hormone secreted by the thyroid gland. Thyroxin exerts a profound influence on the rate of metabolism in the body. It also has an important effect on growth, maturation, differentiation of tissue, water balance, carbohydrate metabolism. It is intimately involved in the functioning of the nervous, muscular, circulatory and reproductive systems and with the activity of other endocrine glands. Disorders of the thyroid gland are so intimately connected with thyroxin production and with iodine metabolism that a great deal concerning the physiological activity of iodine is disclosed through the study of such disorders. The diseased thyroid may produce either a deficiency or an excess of thyroxin. The deficiency state (hypothyroidism) leads, in man, to three pathological conditions—simple or iodine deficiency goiter, cretinism and

myxedema. Overactivity of the thyroid (hyperthyroidism) causes exophthalmic goiter (characterized by protruding eyeballs), among other symptoms. Of these, only simple goiter is caused by iodine deficiency. The condition is characterized by a compensatory enlargement of the thyroid in an attempt to manufacture more of the deficient thyroxin. It responds to dietary supplementation with iodine and is a widespread disease in areas having iodine-deficient soils and water.

Metabolism: Iodine is absorbed from the intestinal tract and circulates, usually as iodides, in the blood. Thyroid tissue exhibits a marked affinity for iodine, absorbing and concentrating the great majority of this material from the blood, and serving as the major storehouse for iodine. Studies with radio-active iodine indicate that absorption of iodine by the thyroid occurs as soon as five minutes following its ingestion. Radio-iodine has also been used to trace the normal metabolic pathway of ingested iodine in animals and in man. By this means the existence in the thyroid of three iodine-containing fractions has been demonstrated, thereby confirming earlier hypotheses that the gland traps inorganic iodide which is utilized for the iodination of tyrosine, an intermediate in the formation of thyroxin. Excess iodine not fixed by the thyroid gland is quickly circulated through the blood stream and eventually eliminated in the urine or, in lesser amounts, through the intestinal tract, in perspiration and in milk.

Deficiency: Iodine deficiency causes simple goiter in man, in certain species of fish and in domestic farm animals. While goiter in farm animals is a common symptom of iodine deficiency, it actually signifies an advanced stage of the disease. The chief economic loss comes from earlier manifestations which are interference with reproductive processes and the birth of weak, deformed offspring often failing to survive. The exceedingly high death-rate of new born sheep has been prevented by iodine prophylaxis as has been the disease among swine known as "hairless pig malady," and various other disorders occurring in sheep, swine, colts, calves, poultry and other livestock. Adequate iodine nutrition of livestock has increased the availability of iodine in the human dietary, expecially with respect to the iodine content of milk. The use of iodized salt, especially in iodine-deficiency areas, has been recommended as a prophylactic measure against the development of goiter in man.

Requirements: A daily allowance of about 0.002 to 0.004 milligrams of iodine per kilogram of body weight has been recommended as desirable. This is equivalent to about 0.15 to 0.30 mg. per day for the average adult (70 kg.). There is considerable evidence that the iodine requirement is heightened during pregnancy and lactation.

Sources: The regular use of iodized salt is a simple means for meeting the dietary iodine requirement. The iodine content of foods and of water is extremely variable depending upon geographical location. In areas where the iodine content of the soil is high it is possible to grow foods relatively rich in iodine and to raise livestock which produce milk and eggs reflecting the superior iodine content of the soil and of their feed.

Fluorine:

In physiological materials fluorine occurs chiefly in bones—especially in fossil bones and teeth—and to a minor extent in all other tissues. It is also present in minute amounts in practically all foods, in most mineral waters and in the soil. Excessive intake of fluorides is associated with specific toxic effects in experimental animals, cattle, swine, sheep and man. Toxic fluorosis is characterized by an accumulation of fluorides in the bones and, eventually, in the tissues. Mild fluorosis in man produces the abnormal dental condition known as mottled enamel. The occurrence of mottled enamel is specifically correlated with the amount of fluoride in the drinking water. It occurs when the water contains 0.9 mg. per liter or more of fluorine. At a level of 2.5 mg. per liter the incidence of mottled enamel is 75-80 per cent; at a level of 6 mg. per liter, the incidence is almost 100 per cent. Mottled enamel occurs especially in the permanent teeth of children exposed during the period of tooth calcification (first eight years of life). It is characterized by discoloration and structural abnormalities of the teeth.

Non-Toxic Levels and Dental Caries: Long before fluorine was identified as the factor in drinking water responsible for mottled enamel, investigators in the field became increasingly aware of an unusual relation between mottled enamel and the incidence of tooth decay. Results of numerous surveys disclosed the striking fact that the teeth of individuals with mottled enamel were remarkably free from the decay or caries usually prevalent in non-affected areas. It soon became apparent that not only are mottled teeth less susceptible to decay, but such teeth *actively resist decay.* Subsequent epidemiological investigations revealed that waters containing traces of fluorine up to a maximum of one part per million would promote the development of caries-resistant teeth without the development of mottled enamel or other tooth defects. A 10-year controlled experiment on the advisability of adding traces of fluorine to municipal drinking water supplies as a caries-preventive measure is now being conducted in the neighboring cities of Kingston and Newburgh, New York. Traces of fluorine have been added to the water of Newburgh, while that of Kingston has been permitted to remain fluorine free for control purposes. The results of this test will provide con-

clusive scientific evidence for the role of fluorine, whatever it may be, in dental health.

Mechanism of Fluoride Inhibition of Caries: Many explanations have been propounded on how fluorine acts in the prevention of tooth decay. Since the etiology of dental caries is even today a matter of considerable dispute and uncertainty, an explanation of the role of fluoride in this phenomenon is not easily developed. There are several general theories concerning the action of fluorine. One view is that fluorine serves as a building stone of the enamel and may be a dietary essential to good teeth as are certain vitamins, calcium and phosphorus. Other investigators believe that fluorine reacts with the tooth substance to form a less soluble tooth material which, therefore, is more resistant to the action of acids which may cause decay. Still another suggestion is that fluorine in trace amounts may act as an enzyme inhibitor preventing the fermentation of carbohydrate residues in the mouth. Such decomposition of carbohydrate is thought to lead to the production of decay-inducing acids. The direct inhibition of acid-producing oral bacteria by fluorine has been advanced as a further possible explanation for the caries-inhibiting influence of this element.

Incorporation of Fluorine into Tooth Structure: Some question exists as to whether fluorine is incorporated into the tooth structure via systemic absorption and diffusion via the blood stream into the dental tissues, or whether it is adsorbed directly onto the enamel during the passage of fluorine-containing foods or water through the mouth. Reports of the successful use of topically applied fluorides in checking caries would seem to favor the latter theory.

Fluorides in Foods: Whether fluorine is a true dietary essential or a pharmacological agent, it is desirable to evaluate the effect of this element when supplied by foods. The available evidence indicates that fluorine in foods exerts the same physiological effects on teeth as fluorine in water. Almost all foods may contain fluorine, depending on the nature of the soil on which they are grown. Physiologically significant non-toxic amounts of fluorine occur in milk, eggs and fish. It is interesting to note that the feeding of additional fluorides to cows and hens results in an increased fluorine content of eggs, but not of milk. Because of its inherent non-toxic level of fluorine and because it comprises an important part of the dietary of children during the critical first eight years, milk may play a significant role in the prevention of dental caries aside from its contributions of calcium, phosphorus and the vitamins.

Bromine:

Bromine occurs as a normal constituent of all tissues. Although its pharmacological properties are well-recognized, it was not until fairly recently that attention was directed to its physiological importance. It is present in significant amounts in certain portions of the brain (hypophysis) and it has been postulated that the future may reveal a biological role of bromine comparable to that of the related halogen, iodine. The metabolism of bromine is similar to that of chlorine, but the two are not physiologically interchangeable.

Physiology: The ingestion of large amounts of bromine is associated with the development of stupor and skin eruptions. Applications of bromine solutions to the skin causes reddening and blistering. If swallowed, it causes inflammation of the mouth, throat and stomach. The industrial use of bromine, like chlorine, may cause poisoning. The biological role of bromides, however, like chlorides, might be of some significance. The fact that the bromine value of blood has been found to be lowered to approximately half the normal value in manic depressive psychoses has aroused speculation as to its possible biological significance. One might conjecture as to whether this decrease in normal bromine values represents a deficiency of an essential element or whether it might indicate a toxic effect due to a possible shift of bromine from the blood to the brain or other organ, thereby inducing an effect similar to the stupor associated with excess bromine intake.

Iron:

The iron content of the human body consists of about four or five grams. Nevertheless this minute amount is vitally important to a number of physiological processes involving cellular respiration and oxidation. Iron is utilized largely for the formation of the red blood cell pigment, hemoglobin. Iron is not destroyed or used up in the body, but is very efficiently conserved and, except for small amounts which may be excreted, is utilized over and over again. For this reason, anemia due to dietary insufficiency of iron does not readily occur unless associated with growth, pregnancy, blood loss or other conditions producing a need for iron above and beyond normal requirements.

Metabolism: The investigation of iron metabolism has centered chiefly around three phases: Absorption, storage and utilization. The absorption of iron from the digestive tract depends largely on two factors: (1) the form in which it is ingested and (2) its "availability" or the completeness with which it can be separated from chemical and physical combinations in foods. It is generally believed that to be absorbed iron must be soluble,

ionizable and ultrafiltrable. Recent investigations have shown clearly that the efficiency of absorption of iron in the ferrous (reduced) form is considerably greater than for the ferric form. The iron in foods is chiefly in the ferric form but it is readily reduced to the ferrous form by the stomach acids. The commonly used "ferrum reductum" (finely powdered metallic iron), a source of iron in fortified foods such as bread, is readily dissolved by stomach acids and is therefore easily available to the body.

Recent studies with radio-iodine in anemic dogs have demonstrated a direct correlation between the amount of iron absorbed and the body need for this element. Further studies along these lines led to the conclusion that the absorption of iron in anemia (due to dietary iron deficiency) is not influenced by the presence of anemia *per se* but is controlled by the degree of depletion of the iron in the tissues—in particular, by the amount of iron present in the cells which line the digestive tract.

Iron is stored in almost all organs of the body, particularly the liver, and when administered to anemic animals, to an even greater extent in the muscles.

The utilization of iron for hemoglobin formation depends upon a large number of factors. Perhaps the most important of these is the presence of minute traces of copper. Calcium has also been demonstrated to be of importance in iron utilization as have such general factors as the state of health and the dietary adequacy of proteins, vitamins and minerals.

Studies with radio-iron have entirely revolutionized the concept that the iron content of the body is regulated by excretion of amounts in excess of physiological requirements. Now it is recognized that iron is essentially a "one-way substance"—it is absorbed (according to the varying needs of the body), but it is not excreted. On the contrary, if made available, excesses are stored when necessary as in growing children and pregnant women.

Function: The normal physiological functions of iron include the formation of hemoglobin and myoglobin (in muscles) and its use in the construction of such respiratory and enzymatic pigments as cytochrome, catalase, Warburg's respiratory pigment and peroxidase.

Deficiency: Iron deficiency anemia occurs most often when requirements are greatest and drains upon the stores of iron are heaviest. Low dietary intakes of iron are regarded as secondary causes of anemia and are believed to result in anemia only when occurring in conjunction with heightened body

requirements. Factors which interfere with absorption from the intestinal tract are also contributory. Ordinary requirements for iron are increased in:

1. Infancy (Exhaustion of iron reserves provided by mother after the fourth month of life; incomplete stores of iron in premature infants and lessened stores in twins who must share available iron.)
2. Childhood (Increased demand for iron during rapid growth due to expanding blood volume.)
3. Adolescence (Iron deficiency anemia (chlorosis) in adolescent girls due to combined demands of growth and menstruation in conjunction with low iron reserves and intake.)
4. Adult women (Due to excessive blood losses of menorrhagia and repeated pregnancies.)
5. Pregnancy (Due to increased blood volume, demands of fetus, loss during lactation.)
6. Life span (Severe blood loss in males and females at any age.)

Requirements: The major importance of a diet containing liberal amounts of iron is not so much to prevent directly the development of anemia, as it is to contribute to or maintain the body reserves of iron for use in emergencies such as those listed above. The average daily intake recommended for adults is 12 mg.; for adolescents and pregnant women, 15 mg.; for infants, 6 mg.; for children from 1 to 13 years of age, from 7 to 12 mg. increasing with age.

Sources: Liver, kidney, beef, egg yolk, oatmeal, molasses, prunes, apricots, raisins, peaches and fortified foods. Milk contains very little iron, but that which is present is in a form which is readily absorbed and utilized. The value of milk in diets designed to improve the iron supply lies in its abundant supply of calcium, minerals and superior protein—factors which markedly influence iron utilization.

Copper:

Copper occurs in all the tissues, the largest amounts being found in the liver, spleen and kidneys. It also occurs in trace amounts in many foods. It was not until 1928, however, that it was recognized that copper has a specific

physiological function. Copper in minute amounts has been shown to be essential to animals and humans for processes involved in hemoglobin formation. Copper is not itself present in the hemoglobin molecule but apparently acts in the capacity of an enzyme.

Deficiency: Lack of copper in the diet is associated with the development of iron deficiency anemia. It has been found that animals reared on a diet consisting exclusively of whole milk, which is very low in iron, develop a nutritional anemia which does not respond to iron therapy alone, but which improves rapidly if traces of copper are also added to the diet. Similar results have been demonstrated with human infants on an iron-deficient exclusive milk diet. Although the infants respond to the addition of iron alone, supplementation with both iron and copper markedly hasten the rate of recovery. Copper has also been demonstrated to be an efficient prophylactic agent against the anemia of infancy, babies receiving copper and iron supplements showing hemoglobin values 19 per cent above those in other infants.

In domestic animals the addition of copper and iron to iron-deficient diets not only protects against nutritional anemia but also exerts beneficial effects on growth and reproduction. In the nutritional anemia of suckling pigs either iron alone or iron and copper stimulates the formation of hemoglobin. The anemia common to yearlings and heifers' suckling calves responds to iron therapy only when supplemented with copper salts.

Copper deficiency has also been related to the development of a disease of lambs known as *enzootic ataxia* or "swayback" which is characterized largely by nervous symptoms. It is prevented by feeding copper to the pregnant ewe. "Falling disease" in cattle is another disease which has been reported to occur in Australia as a result of chronic copper deficiency. The disease is manifested by staggering, falling and instantaneous death. Combined copper and iron deficiency in animals also occurs in parts of Florida.

In new-born calves the liver store of copper is about eight times that of the adult. In humans it has been found that the liver stores of copper are less in anemic infants than in normal infants.

Requirements: Copper is apparently essential for man and most animals in the utilization of iron for hemoglobin formation. The average human requirement is not known but has been estimated to be about 2 milligrams per day or less. A suggested optimum amount for children is 100 micrograms per kg. of body weight; for adults about 60 micrograms per kg.

Sources: Important food sources of copper include liver, oysters, bran, shrimp, lobster, sweet chocolate, mushrooms, cereal grains, leafy and legum-

inous vegetables. Egg yolk, an excellent source of nutritionally available iron, contains copper in a form which is not readily utilized by the body.

Cobalt:

Cobalt was established as a dietary essential about ten years ago. Excess amounts, however, produce an abnormal increase in blood cells (polycythemia). The use of cobalt supplements has been demonstrated to be of specific value in the treatment of a fatal type of nutritional anemia ("pine disease") occurring in sheep and cattle. The condition has been reported chiefly in Australia and New Zealand and in certain areas in Florida, Wisconsin, Michigan and the New England States. It is thought to reflect inherent deficiencies in the local pastures. The symptoms of pine disease include progressive emaciation, loss of appetite and pallor of the visible membranes. There is usually also an associated reduction in red blood cells and hemoglobin values. Treatment with cobalt salts has been reported to be effective in restoring appetite and weight and in correcting the anemia.

The nutritional anemia of cud-chewing animals was formerly treated with iron compounds. More recently it has been found that traces of cobalt are present in all of the compounds which are effective in treating these anemias. It has been shown, further, that the anemia can be cured and even prevented by giving cobalt salts without iron. The efficacy of cobalt salts is increased in the presence of minute traces of nickel. A dose of 1 mg. per day of cobalt for two weeks has been reported to be curative of nutritional anemia in sheep. The role, if any, of cobalt in the nutritional anemia of man has not yet been demonstrated. The theory has been advanced that cobalt functions by virtue of its effect on rumen bacteria, enabling them to produce B complex vitamins needed by the animal. Cobalt deficiency has been detected only in ruminants. The feeding of cobalt has been found to be more effective than injecting it into the blood stream, while the injection into the blood of a group of the B complex vitamins overcame the effects of cobalt deficiency.

Zinc:

Zinc has been shown to be an essential element in plant and animal nutrition. It is present in all tissues and foodstuffs in amounts comparable to or somewhat less than iron. Contrary to previous opinion, zinc was shown about two decades ago to be non-toxic.

Deficiency: A deficiency of zinc in rats has been found to result in impaired growth, certain pathological changes and a depression of the action of the phosphatase enzymes. Similar effects have been observed in mice. In

addition, a marked reduction was observed in the catalase activity of the liver and kidneys (but not of blood), thus adding two additional enzyme systems to the small list of those affected by zinc deficiency. The function of zinc in influencing catalase, however, is believed to be an indirect one firstly, because no zinc has been demonstrated in any of the crystalline catalase enzymes and secondly, because the addition of zinc to tissue preparations from zinc-deficient mice does not increase or restore the catalase activity. Mice on a zinc-deficient diet exhibited a mortality rate of 18 per cent over a period of eight weeks as compared with 100 per cent survival of control animals.

Functions: Zinc is essential for growth in animals and for the efficient operation of certain enzyme systems. The rate of absorption of carbohydrates and proteins from the gastro-intestinal tract is influenced by the concentration of zinc in the diet. The delay in absorption of these nutrients occurring in zinc-deficient rats leads to a decrease in the efficiency of converting foodstuffs into body tissues.

The universal presence of zinc in crystalline insulin, regardless of the method of preparation, in various commercial preparations of insulin and in the pancreas has led to speculation as to a possible relation between zinc and this hormone. In view of the fact that the zinc content of the pancreas in diabetics is about one-half that of non-diabetics, it has been suggested that the zinc in the pancreas may be concerned in some way with the storage and utilization of insulin.

NEWS DIGEST

CHOLINE AND CANCER—Insufficiency of the B vitamin, choline, has long been known to be a factor in the cause of fatty livers and liver cirrhosis in experimental animals and possibly in man. Recent animal experiments have shown that cirrhosis of the liver is soon followed by cancer of the liver in all cases. Since cancer of the liver in humans also frequently follows cirrhosis, these experiments assume added significance. The animals on the choline deficient diet were found to develop not only liver cancer, but malignancies of the lungs and other tissues as well. Liver cancers occurred in 30 per cent of the animals on the choline-low diet; 38 per cent developed lung cancers; 10 per cent developed malignant tumors under the skin or in muscle tissues. . . . Only slightly more than one-fifth of the animals failed to develop cancers on this diet. None of the control animals receiving the same diet plus choline were affected. Of the many attempts to link cancer to diet, this is believed to be the first in which cancer has been produced in experimental animals as a result of a specific dietary deficiency. *Science News Letter,* Oct. 26, 1946.

THREONINE VALUES OF FOODS — The microorganism S. fæcalis (also known as S. lactis R) has been used successfully as a means for assaying the threonine content of foods. Studies on the nutritional requirements of this organism, prominent in the discovery of folic acid, indicate that 13 amino acids are essential for its metabolism. Four other amino acids were found to be non-essential but to have stimulating effects. The essentiality of the amino acid, threonine, made possible the development of an assay method using this microorganism. By the use of this method the following threonine values were obtained: meats, 4.1 to 4.7; casein, 3.7; lactalbumin 5.0; soybean oil meal 3.9; whole corn 4.4 per cent threonine in the protein (calculated to 16 per cent nitrogen). *J. Biol. Chem. 102,* 69, (1946).

DEHYDRATED VEGETABLE WASTES — Vegetable wastes such as outer leaves and tops have been found to be sources of highly nutritious animal foods or supplements to human diets. A meal made from the waste outer leaves of Florida celery, for example, has proved superior to alfalfa-leaf meal as poultry or livestock feed. Moreover, alfalfa-meal has to be imported into Florida while the celery leaves are an abundant waste product there. Similarly, in Pennsylvania it has been found that the outer leaves, tops and vines of broccoli and other vegetables contain more and better protein, riboflavin and carotene than parts of the plant normally eaten. When dehydrated and milled, these discards make highly nutritious meals that can be used to feed poultry, animals and human beings. Even the grass growing on well-fertilized golf courses has been found to contain a high percentage of protein. *J. Am. Diet. Assoc. 22,* 1075 (1946).

TURKEY MEAT — Tests reveal that turkey meat provides not only protein and fat but significant amounts of thiamine. The meat just under the skin is richer in this vitamin than that nearer the bone. During roasting it has been found that dark meat loses slightly more than one-half of the original thiamine content; white meat more than one-third. Reheating left-over turkey meat does not result in any marked further loss of thianine. *J. Am. Diet. Assoc. 22,* 1087 (1946).